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FURTHER OBSERVATIONS ON THE FORMATION OF SIGMA PHASE IN A NICKEL-BASE SUPERALLOY (IN-100)

by Robert L. Dreshfield and Richard L. Ashbrook

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16. Abstract

Sigma-free, moderately, and very sigma prone cast IN-100 were exposed at 1550° F (843° C) for 250 and 2500 hours to permit sigma to form. As sigma increased, rupture life, tensile strength and ductility decreased. Yield strength at room temperature increased after exposure for 250 hours. Exposure times of 2500 hours caused the yield to approach or fall below the as cast value. Sigma isothermal transformation curves were prepared for wrought and cast IN-100 having essentially the same compositions. Wrought material exposed in a stress gradient at 1550° F (843° C) was examined for a stress effect on sigma formation.

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SUMMARY

The primary purpose of this work was to determine the effect of sigma phase, formed before testing, on the mechanical properties of IN-100. Fine grained investment cast material was prepared from a single master heat to which only aluminum and titanium were added during remelting to provide three alloys with varying tendencies toward sigma formation. This material was exposed for 250 and 2500 hours at 1550° F (843° C) before mechanical testing. These exposures produced sigma in the alloys which were sigma prone.

Room temperature ultimate tensile strength and ductility of cast IN-100 decreased with exposure time at 1550° F (843° C). For expsoures of 2500 hours, ultimate tensile and yield strengths and ductility decreased with increasing sigma. At 1400° F (760° C) ultimate tensile and yield strengths were usually greater than at room temperature. The ductility of sigma prone materials, measured at 1400° F (760° C), decreased with exposure time, but the opposite was true of sigma free material.

Stress rupture tests were run at temperatures from 1360° to 1800° F (738° to 982° C). For the sigma prone materials, the rupture life decreased with increasing tendency toward sigma formation and with increasing exposure time.

Unstressed isothermal transformation curves for the start of sigma formation were developed for wrought and cast IN-100. When wrought IN-100 having a moderate tendency toward sigma formation was exposed 1008 hours at 1500° F (816° C) under stresses from 2500 to 35 000 psi (17 to 241 MN/m^2), increasing stress suppressed sigma formation.

INTRODUCTION

To study the effect of sigma phase formation in a cast nickel base superalloy three special compositions of IN-100 having varying tendencies toward sigma formation were prepared. Although IN-100 is commercially available in compositions which will not form significant quantities of sigma phase during long-time exposure under stress (ref. 1), sigma can form in certain ranges (refs. 1 and 2) of the Aerospace Materials Specification for IN-100, AMS 5397 (ref. 3). Three special compositions were formulated so that one would be sigma free, one moderately sigma prone, and one very sigma prone when exposed to elevated temperatures. This variation in tendency toward sigma formation was achieved by adding only aluminum and titanium to a single master heat during remelting. The effect of sigma formation on as-cast mechanical properties and isothermal transformation curves for these alloys were reported in reference 2.

This report discusses results of three aspects of sigma phase formation in a nickel-base superalloy. First, the effect on mechanical properties of sigma phase when present before testing is discussed. Second, isothermal transformation curves are developed for a wrought alloy series having compositions similar to those of the casting alloys. In this report, these alloys will be called wrought IN-100. Finally, the results of an experiment designed to study the influence of applied stress on the rate of sigma formation are discussed.

To study the effect of sigma on mechanical properties of IN-100 when sigma is present before testing, fine grained castings from the same lot of castings described in reference 2 were exposed to a 1550° F (843° C) temperature prior to being tested. Exposure times were 250 and 2500 hours. After exposure, stress-rupture tests were run at temperatures from 1360° to 1800° F (738° to 982° C). Tensile tests were run at room temperature and 1400° F (760° C).

The wrought alloys were prepared from ingots to which aluminum and titanium additions had been made similar to those made to the cast alloys. The same master heat of IN-100 was used to make both cast and wrought alloys. Isothermal transformation curves for the wrought alloys were determined and compared to curves for the cast alloys.

Tensile specimens having an hourglass shape were prepared from a sigma prone composition of a wrought alloy. These were exposed under stress to temperatures of 1500° and 1550° F (816° and 843° C) to evaluate the influence of applied stress on the rate of sigma formation.

PROCEDURE

Materials

Cast. - The fine grained vacuum melted investment cast specimens used in this work were previously described in reference 2. During remelting for casting, additions of aluminum (Al) plus titanium (Ti) were made to material from a single master heat. Additions were chosen to provide castings with three different propensities toward sigma formation. The specific additions were determined by a modification (ref. 2) of the phase computation method of Boesch and Slaney (ref. 4). Compositions and average electron vacancy concentration numbers ($\overline{N}_v$) of arbitrarily selected remelt heats are shown in table I. The higher the Al plus Ti content, the higher the average electron va-

TABLE I. - CHEMICAL ANALYSES OF CAST AND WROUGHT IN-100

Form	Element, wt. % (balance Ni)											[a]Average electron vacancy concentration, $\overline{N}_v$
	Co	Cr	Al	Ti	Mo	V	Si	Fe	Zr	C	B	
Low $\overline{N}_v$ (sigma free)												
Cast	13.58	10.26	4.95	4.10	3.45	0.96	0.08	0.07	0.02	0.160	0.014	2.27
	13.48	10.13	5.03	4.22	3.65	1.01	.08	.14	.04	.176	.015	2.31
Wrought	13.73	10.26	4.95	4.08	3.66	0.96	0.09	0.07	0.03	0.157	0.014	2.29
Medium $\overline{N}_v$ (moderately sigma prone)												
Cast	13.29	10.15	5.47	4.28	3.51	0.96	0.10	0.07	0.03	0.160	0.014	2.47
	13.35	10.13	5.51	4.30	3.60	.96	.10	.07	.03	.164	.013	2.51
Wrought	13.41	10.15	5.36	4.09	3.58	0.96	0.09	0.12	0.02	0.157	0.012	2.40
High $\overline{N}_v$ (very sigma prone)												
Cast	13.22	10.11	5.55	4.59	3.50	0.96	0.11	0.06	0.03	0.157	0.014	2.59
	13.29	10.13	5.65	4.78	3.53	.98	.09	.08	.03	.158	.012	2.71
Wrought	13.42	10.13	5.46	4.63	3.58	1.01	0.09	0.07	0.02	0.155	0.013	2.59
AMS 5397[b]												
Cast												
Minimum	13.00	8.00	[c]5.00	[c]4.50	2.00	0.70	----	----	0.03	0.15	0.01	----
Maximum	17.00	11.00	6.00	5.00	4.00	1.20	0.15	1.00	.09	.20	.02	----

[a]Method of Woodyatt, Sims, and Beattie; critical $\overline{N}_v \approx 2.46$ (ref. 2).
[b]Ref. 3.
[c]Al + Ti > 10.0.

cancy concentration ($\overline{N}_v$), and the greater the tendency to form sigma. No sigma was observed in any as-cast material.

Wrought. - Three 100-pound (45.5-kg) vacuum induction heats were melted by a forging supplier. The starting material for each heat was a portion of the same master heat used for making the investment castings. Appropriate additions of Al plus Ti resulted in three propensities toward sigma formation. The induction melted IN-100 was cast into 4-inch (10.2-cm) diameter ingots. These ingots were vacuum arc remelted to 5-inch (12.7-cm) diameter ingots by a specialty steel producer. After cropping, the ingots were canned in steel pipe for extrusion. Extrusion was done at 2050° F (1121° C) to a diameter of about $3\frac{1}{8}$ inch (7.92 cm).

The extrusions were forged into pancakes in three flattening operations. In preparation for flattening the unsound ends of the extrusions were cut back to sound metal and the extrusions were cut into thirds. Flattening was done at 2050° F (1121° C).

Before each flattening, the forgings were cleaned by grinding and sandblasting. They were then coated with a protective ceramic paint and wrapped in a ceramic insulating cloth. Forging was done with heated dies and between 1/8-inch (0.32-cm) steel covers. The forgings were cut in half longitudinally before the last reduction.

The following nominal reductions were used:

(1) $3\frac{1}{8}$-inch (7.92-cm) diameter extrusion to $1\frac{3}{4}$-inch (4.45-cm) pancake

(2) $1\frac{3}{4}$-inch (4.45-cm) pancake to 1-inch (2.54-cm) pancake

(3) 1-inch (2.54-cm) pancake to 5/8-inch (1.59-cm) pancake (fig. 1)

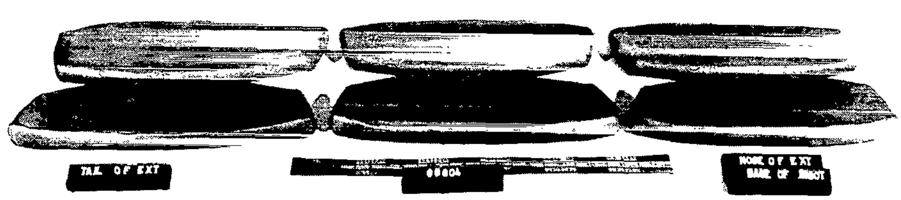

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Figure 1. - Wrought 5/8-inch (1.59-cm) thick pancakes of IN-100 (courtesy of Wyman-Gordon Co.).

The yield was about 30 pounds (13.6 kg) of forgings per 100 pounds (45.5 kg) of starting material.

Table I also lists chemical analyses and calculated $\overline{N}_v$s of the extrusion billets used to produce the forgings. The analyses were very similar to the cast analyses and so were the $\overline{N}_v$s. However, the $\overline{N}_v$ of the medium $\overline{N}_v$-wrought material was slightly lower, 2.40, than the 2.47 to 2.51 calculated for cast medium $\overline{N}_v$.

Heat Treatment

Cast materials. - To be able to determine the effect of preexisting sigma on the mechanical properties of IN-100, different quantities of sigma were required. Cast test bar blanks were exposed at 1550° F (843° C) in argon for 250 and 2500 hours. Bars of each of the three $\overline{N}_v$ levels were heated together.

Wrought materials. - The wrought material which was to be used for establishing sigma isothermal transformation curves was first heat treated in a schedule typical of that used for a wrought nickel base alloy. The treatment was 2200° F (1204° C) for 4 hours, 2000° F (1093° C) for 4 hours, 1550° F (843° C) for 16 hours, and finally 1400° F (760° C) for 24 hours. All specimens were heated under argon and air cooled to room temperature after each heating cycle.

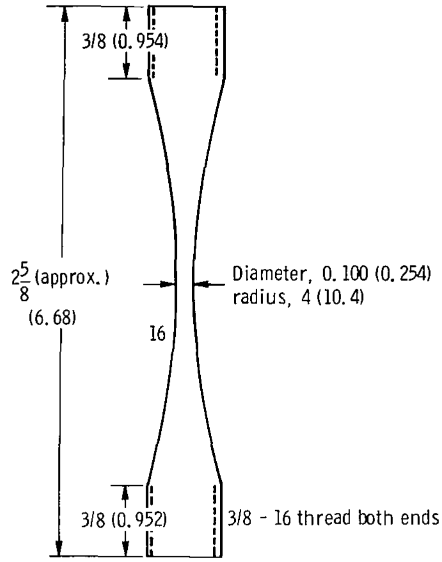
Unstressed isothermal transformation. - Isothermal transformation curves for the start of sigma formation were established both for as-cast and for heat treated wrought material. Although curves for as-cast material were reported in reference 2, for this report data were obtained at additional time-temperature conditions. Material from the gage sections of tensile bars was used to make the cast isothermal transformation specimens. Excess wrought material from pancakes cut for tensile specimens was solution treated and aged before exposure at the temperatures chosen for isothermal transformation. Cast and wrought specimens were heated under argon without applied stress at temperatures from 1300° to 1800° F (704° to 982° C) and times from 1 to 5000 hours.

Exposure under stress. - Hourglass shaped specimens (fig. 2(a)) were machined from wrought medium $\overline{N}_v$ material heat treated in the same way as the wrought isothermal transformation specimens except that they were solution treated at 2215° F (1213° C) to dissolve more massive gamma prime than was dissolved at 2200° F (1204° C). The varying cross section permitted stress to vary by a factor of approximately 14 from the minimum to the maximum section.

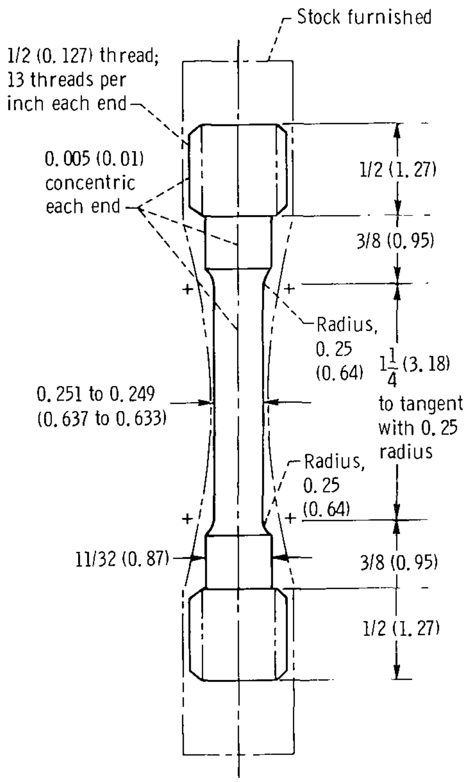
Three specimens were exposed under load to determine the effect of stress on sigma formation. One specimen was exposed 1008 hours at 1500° F (816° C) with a maximum stress of 35 000 psi (241 MN/m^2). Two were exposed at 1550° F (843° C) - one for 384 hours at a maximum stress of 35 000 psi (241 MN/m^2) and one for 1008 hours at a maximum stress of 21 000 psi (144 MN/m^2).

Mechanical Testing

Tensile tests and constant load stress-rupture tests were conducted on the alloys in accordance with appropriate ASTM recommended practices. The same test bar design was used for both tensile and stress rupture testing as was used in reference 2. Cast



(a) Stress gradient bar.



(b) Mechanical test bar.

Figure 2. - Test specimens. Dimensions are in inches (cm).

specimens were ground to a nominal 1/4-inch- (0.6-cm-) diameter at the test section (fig. 2(b)). A gage length was defined by punch marks 1.75 inches (4.44 cm) apart placed on the shanks of the specimen. The effective gage length was taken as the distance between the base of the fillets. Elongation was calculated from the following equation:

$$\text{Percent E} = \frac{\text{Final GL} - \text{Original GL}}{\text{Effective GL}} \times 100 \tag{1}$$

where GL is gage length.

Stress-rupture specimens were heated to the test temperature in 3 to 5 hours and soaked an additional 1 to 2 hours prior to loading. Care was taken not to exceed the test temperature during heating. Stress-rupture tests were conducted between 1360° and 1800° F (738° and 982° C) at stresses of 95 000, 40 000, and 20 000 psi (654, 276, and 138 MN/m^2).

Tensile specimens were pulled at room temperature and at 1400° F (760° C).

Metallography

For general examination a swabing etchant of the following composition was used: 33 parts water, 33 parts nitric acid, 33 parts acetic acid, and 1 part hydrofluoric acid. This etch reveals gamma prime and sigma. The sigma is optically active, and can be seen more easily under polarized light. A modified Murakami's etch was used for the isothermal transformation specimens. This etch was made from equal volumes of the two solutions: 10 grams of potassium ferrocyanide in 90 milliliters of water, and 10 grams of potassium hydroxide in 90 milliliters of water. Murakami's etch darkens sigma and carbides, but has little effect on gamma or gamma prime; sigma is made optically active. All photomicrographs in this report were made using bright field illumination.

RESULTS AND DISCUSSION

Effect of Sigma on Mechanical Properties

Tensile. - Figure 3 shows the effect of exposure at 1550° F (843° C) and of $\overline{N}_v$, or tendency to form sigma, on the average room temperature tensile properties of fine grained cast IN-100. The individual data points are shown in table II. Exposure for longer times progressively decreased the ultimate tensile strength at each of the three

TABLE II. - EFFECT OF EXPOSURE AT 1550° F (843° C) ON TENSILE PROPERTIES OF FINE GRAINED CAST IN-100 AT ROOM TEMPERATURE AND 1400° F (760° C)

Room temperature

Alloy type, $\overline{N}_v$	Ultimate tensile strength		0.2-Percent yield strength		Elongation, percent	Reduction in area, percent
	psi	MN/m^2	psi	MN/m^2		
As-cast						
Low	138.1×10^3	952	101.1×10^3	697	9	10
	145.6	1004	102.6	707	15	12
Medium	151.5×10^3	1045	107.3×10^3	740	12	11
	154.9	1068	117.7	812	7	6
High	131.4×10^3	906	96.7×10^3	667	6	7
	153.7	1060	(a)	(a)	12	11
Exposed 250 hr						
Low	140.6×10^3	970	129.6×10^3	894	5	4
	132.3	912	110.4	761	8	6
Medium	136.9×10^3	944	120.4×10^3	830	4	3
	137.6	949	121.4	837	3	2
High	130.2×10^3	898	115.5×10^3	796	2	1
	110.0	758	109.0	752	1	1
Exposed 2500 hr						
Low	129.3×10^3	892	112.0×10^3	772	4	4
	132.8	916	101.0	696	9	7
Medium	116.9×10^3	806	101.0×10^3	696	2	2
	119.0	821	101.6	701	1	2
High	121.4×10^3	837	95.7×10^3	660	1	2
	111.8	771	97.2	672	1	2

Temperature, 1400° F (760° C)

As-cast						
Low	144.0×10^3	993	(a)	(a)	7	7
	146.0	1007	(a)	(a)	11	11
	140.0	965	124.2×10^3	856	6	6
	138.9	958	112.4	775	6	6
Medium	154.5×10^3	1065	(a)	(a)	7	5
	145.2	1001	(a)	(a)	3	2
	145.2	1001	106.4×10^3	734	6	8
	154.6	1066	122.2	843	14	11
	138.7	956	119.8	826	5	4
High	136.9×10^3	944	(a)	(a)	2	2
	145.4	1003	(a)	(a)	3	3
	148.9	1027	115.8×10^3	798	3	5
	145.8	1005	114.9	792	11	14
Exposed 250 hr						
Low	143.0×10^3	992	110.0×10^3	765	16	15
	149.0	1033	119.8	826	4	4
	142.2	980	124.6	859	7	7
Medium	155.2×10^3	1070	123.9×10^3	854	5	6
	145.0	1000	127.1	876	1	1
	138.9	958	123.4	851	11	9
High	139.7×10^3	964	132.0×10^3	913	1	1
	141.3	974	122.2	843	1	1
Exposed 25 000 hr						
Low	137.7×10^3	949	118.7×10^3	818	3	3
	133.9	923	98.6	680	20	20
	139.4	961	118.8	819	6	5
Medium	142.4×10^3	982	120.5×10^3	831	2	2
	141.3	974	118.3	816	2	2
High	139.7×10^3	963	119.8×10^3	826	2	2
	140.5	969	122.2	843	2	2

[a]Not determined.

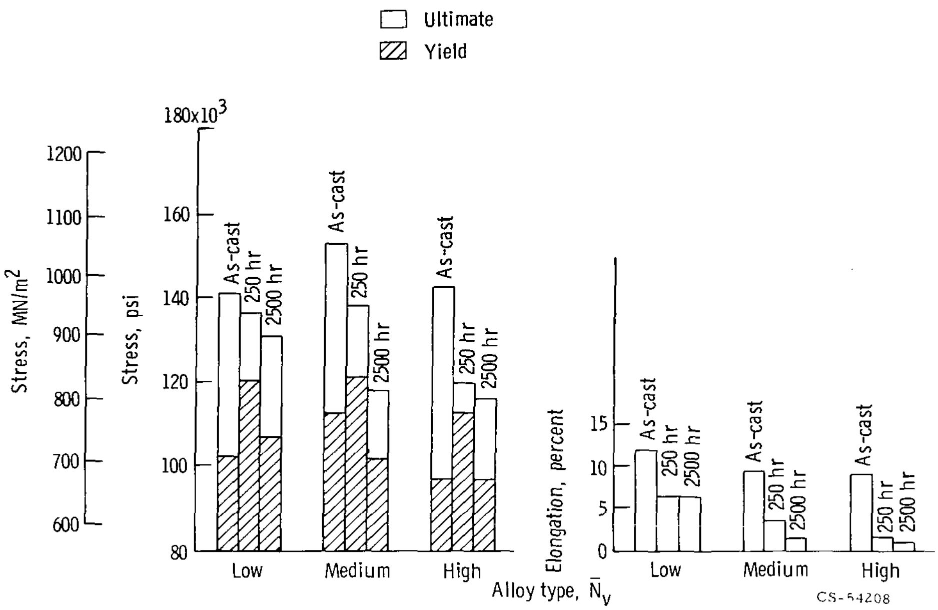
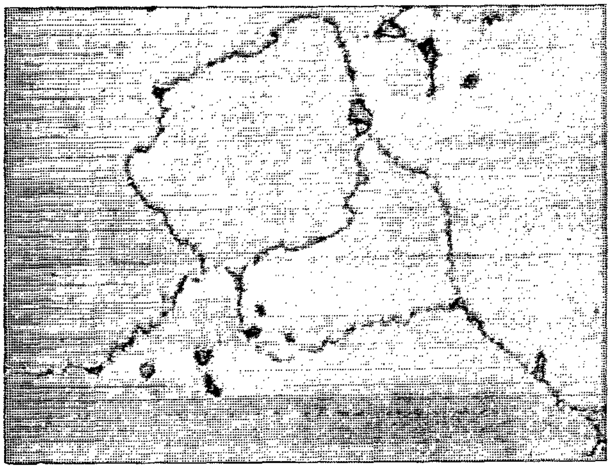


Figure 3. - Effect of exposure at 1550° F (843° C) on average room temperature tensile properties of cast IN-100.

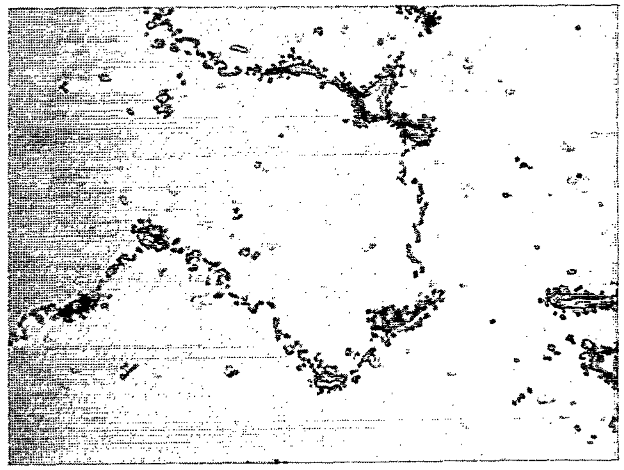
$\overline{N}_v$ levels considered. After 2500 hours exposure at 1550° F (843° C) the ultimate strength decreased with increasing tendency toward sigma formation. The drop in strength after exposure may be related to a corresponding drop in ductility. For example, the elongation of moderately sigma prone (medium $\overline{N}_v$) IN-100 changed from 9.5 percent as-cast to 1.5 percent and ultimate tensile strength from 153 000 to 118 000 psi (1055 to 806 MN/m^2) after 2500 hours exposure at 1550° F (843° C). Most of the loss of ductility of the medium and high $\overline{N}_v$ material was clearly related to sigma formation. The sigma prone materials fractured by transgranular cleavage. Even though a dendritic pattern was evident, the fracture was planar within individual grains. This is typical of the "inter-sigmatic" fracture described by Ross (ref. 1).

Figure 4 shows the microstructures of high, medium, and low $\overline{N}_v$ cast IN-100 after 250 and 2500 hours exposure. No sigma was evident in the low $\overline{N}_v$ alloy. A moderate amount of sigma formed in the medium $\overline{N}_v$ alloy in 250 hours. Substantially more formed in 2500 hours. The high $\overline{N}_v$ alloy, on the other hand, formed almost as much sigma in 250 hours as the medium $\overline{N}_v$ did in 2500 hours. Further exposure to 2500 hours increased the sigma in the high $\overline{N}_v$ alloy only slightly. The loss of room temperature tensile strength and ductility (comparing sigma prone alloys to sigma free ones with like exposures) appears to be associated with these relative amounts of sigma present. As will be discussed later, this same relation of sigma and degradation of properties also seems to hold true for rupture life.

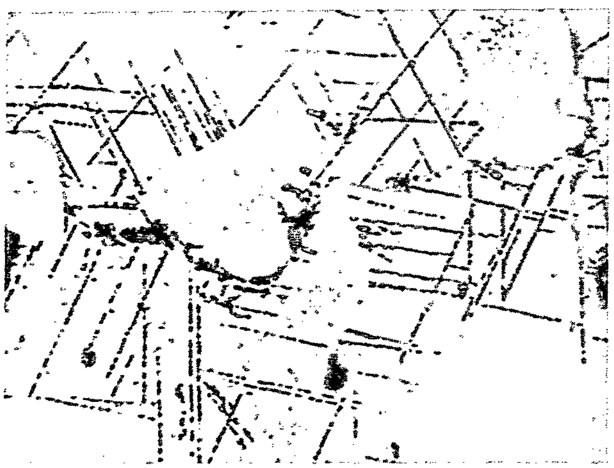
The room temperature yield strength of all three materials increased after being



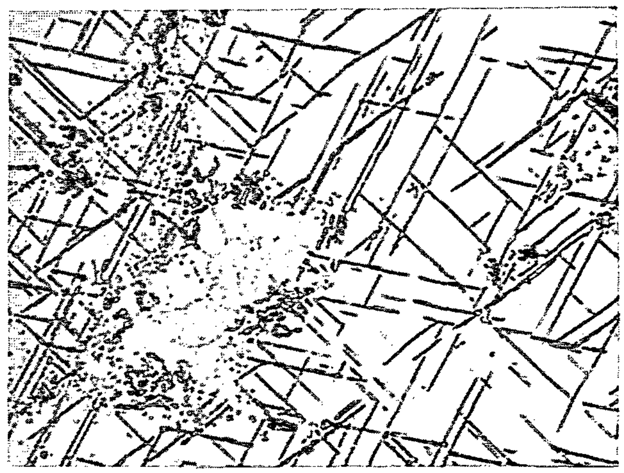
(a) Low $\bar{N}_v$; 250 hours.



(b) Low $\bar{N}_v$; 2500 hours.

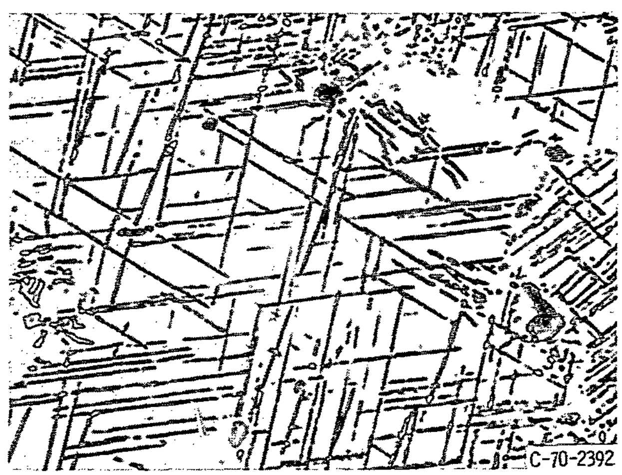


(c) Medium $\bar{N}_v$; 250 hours.



(d) Medium $\bar{N}_v$; 2500 hours.

(e) High $\bar{N}_v$; 250 hours.



(f) High $\bar{N}_v$; 2500 hours.

Figure 4. - Effect of exposure time at 1550° F (843° C) on sigma formation in cast IN-100. Etchant, modified Murakami's solution; X750.

exposed for 250 hours. Overaging appears to have occurred in material exposed for 2500 hours (fig. 3) causing the yield strength to approach or drop below the as-cast yield strength. Because this occurred in all three alloys we assume that the aging reactions do not involve sigma. The phenomenon is assumed to be caused by carbide reactions or the precipitation of secondary gamma prime.

The increase in the gamma prime formers, Al and Ti, was expected to increase yield strength with increasing $\overline{N}_v$. This did not occur. The yield strength of the high $\overline{N}_v$ material was lower than that of low or medium $\overline{N}_v$ material in each of the three conditions tested.

The effect of exposure at 1550° F (843° C) on tensile properties measured at 1400° F (760° C) is shown in figure 5. The individual data points are also listed in table II. The

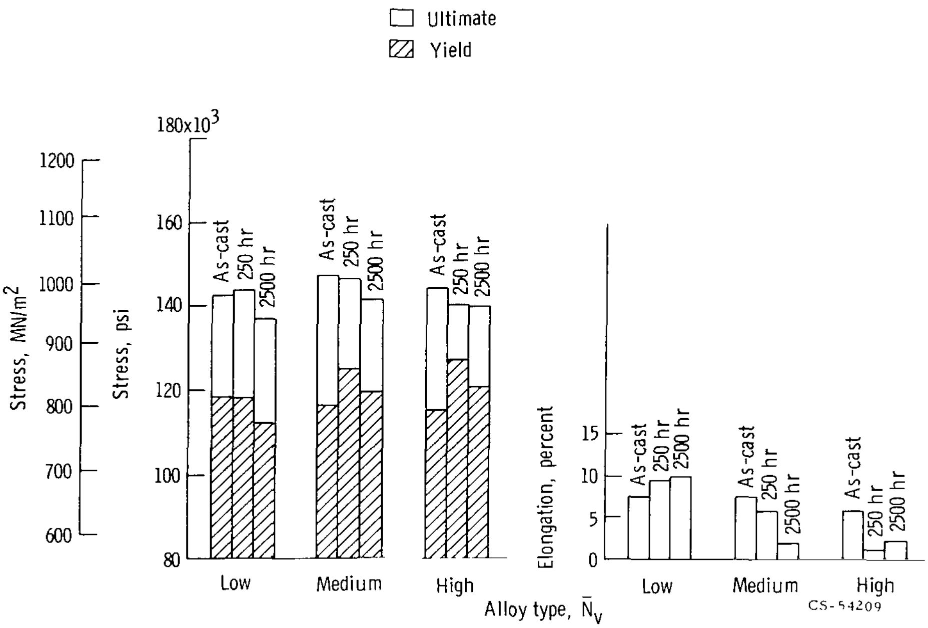


Figure 5. - Effect of exposure at 1550° F (843° C) on average tensile properties of cast IN-100 at 1400° F (760° C).

ultimate tensile strength of all three alloys was changed little by this exposure. Furthermore, it varied little with tendency to form sigma. The ultimate tensile strength for all three alloys was slightly lower than the as-cast strength after 2500 hours exposure.

The yield strength at 1400° F (760° C) shows no strong trend either with exposure time or with alloy type.

The elongation of the sigma-free alloy increased from $7\frac{1}{2}$ percent as-cast to 9 percent after aging 2500 hours. The sigma prone alloys' elongations decreased with exposure; however, the elongation of highly sigma prone alloy was slightly higher after 2500 hours exposure than after 250 hours.

Most of the trends previously cited for room temperature tensile tests are also apparent in the 1400° F (760° C) data. The yield strength tends to be greatest after the 250-hour exposure. Although the change is not large, the ultimate tensile strength tends to decrease with increasing exposure time. Increasing sigma forming tendency by increasing Al and Ti decreases ductility at all exposure times studied. These trends become more apparent when both room temperature and 1400° F (760° C) tensile data are considered together than when only the 1400° F (760° C) data are considered.

In most conditions the ultimate tensile and yields strengths at 1400° F (760° C) were greater than at room temperature. This is in keeping with the reported behavior of IN-100 and other nickel base superalloys which form large amounts of gamma prime (ref. 5) and which reach maximum strength at about 1400° F (760° C).

Stress-rupture. - The effects of exposure time and sigma forming tendency on the stress-rupture life of IN-100 are shown in figures 6 to 9. Figure 7 shows the effect of sigma forming tendency and of exposure time on rupture life by showing the ratio of life of exposed materials to the life of as-cast material for a range of test temperatures. Figures 8 and 9 show the same data plotted as the ratio of the life of a given alloy to the life of sigma free material in the three conditions of exposure. This emphasizes the effect of sigma forming tendency on the stress rupture properties. The rupture data are from table III. The values plotted in figures 6 to 9 for tests at 40 000 psi (276 MN/m^2) were calculated from times which were obtained by least squares fitting regression equations to the data in table III. The resulting equations were then solved for time, given a temperature. Except for the moderately sigma prone alloy as-cast and exposed 250 hours, the following linear equation fitted the data satisfactorily:

$$\log (\text{time}) = A + B (\text{temperature})$$

In the two exceptions cited the following parabola was fitted to the data to obtain a better fit:

$$\log (\text{time}) = A + B (\text{temperature}) + C (\text{temperature})^2$$

The separate points in figures 7 to 9 for stresses other than 40 000 psi (276 MN/m^2) were obtained from the geometric means of data in table III. Only the 40 000 psi (276 MN/m^2) stress rupture results are plotted in figure 6.

The stress-rupture experiments were conducted to shed further light on the mechanism responsible for the rupture life degradation associated with sigma phase. Two hypotheses were considered. Our first hypothesis was that only carbide or gamma-gamma

TABLE III. - STRESS RUPTURE DATA OF CAST IN-100

Alloy type, $\overline{N}_v$	Test condition		Condition								
	Temperature, $^{\circ}F$ (C)	Stress, psi (MN/m^2)	As-cast			250 hours at 1550° F (843° C)			2500 hours at 1550° F (843° C)		
			Life, hr	Elongation, percent	Reduction in area, percent	Life, hr	Elongation, percent	Reduction in area, percent	Life hr	Elongation, percent	Reduction in area, percent
Low	1360 (738)	95 000 (654)	203.3	4	3	269.3	10	12	425.4	7	8
			277.3	5	5	165.9	6	8	242.3	5	6
Medium			223.0	3	3	208.5	9	11	163.5	9	9
			225.5	6	6	165.2	6	10	133.0	5	6
			131.2	2	2	------	--	--	------	--	--
High			71.9	3	3	50.9	2	3	29.9	2	2
			138.5	4	2	74.0	5	6	73.0	5	6
	1475 (802)	40 000 (276)	1494.0	11	11	------	--	--	------	--	--
	1475 (802)	40 000 (276)	1200.0	(a)	14	------	--	--	------	--	--
Low	1550 (843)	40 000 (276)	2372.7	(a)	9	2637.4	(a)	12	2234.3	8	7
			861.3	11	9	2103.4	9	8	2140.6	6	6
			3076.1	11	10	------	--	--	------	--	--
			2774.8	10	9	------	--	--	------	--	--
Medium			714.2	11	13	629.9	8	10	266.0	9	12
			815.8	6	10	641.8	7	12	277.2	13	15
High			320.8	5	3	158.1	9	11	92.9	7	8
			319.6	6	9	144.9	8	6	115.1	11	18
Low	1575 (857)	40 000 (276)	1776.0	9	9	1320.2	(a)	11	1362.3	9	9
			1546.5	(a)	(a)	1136.1	(a)	10	1510.3	10	8
Medium			------	--	--	481.0	8	10	123.6	12	16
			------	--	--	590.0	6	9	150.3	10	14
High			------	--	--	95.6	8	11	56.6	7	9
			------	--	--	------	--	--	117.4	9	15
Low	1625 (885)	40 000 (276)	423.2	11	8	------	--	--	------	--	--
			456.3	11	9	------	--	--	------	--	--
Medium			396.6	9	9	------	--	--	44.1	12	15
			378.4	9	10	------	--	--	38.1	11	11
High			130.9	5	5	------	--	--	20.3	10	14
			86.1	2	2	------	--	--	14.0	10	14
Low	1675 (913)	40 000 (276)	127.9	8	9	108.1	12	10	76.9	12	15
			115.7	9	6	143.7	14	13	92.9	(a)	13
			67.2	11	9	------	--	--	------	--	--
Medium			118.4	9	9	69.8	9	10	11.7	9	12
			134.3	8	10	74.3	5	4	13.8	11	12
High			61.1	6	6	10.3	9	11	4.9	9	11
			27.8	3	4	11.2	7	10	6.9	9	15
			------	--	--	12.0	7	8	------	--	--
Low	1800 (982)	20 000 (138)	242.0	11	13	250.1	9	15	184.2	11	13
			210.6	13	18	246.6	10	15	186.5	13	14
Medium			268.8	6	8	273.3	9	10	123.4	12	16
			293.0	8	7	255.9	5	5	103.1	10	12
High			280.0	7	6	130.0	7	6	49.1	7	7
			214.8	8	8	99.3	3	4	49.7	11	9

[a]Not available.

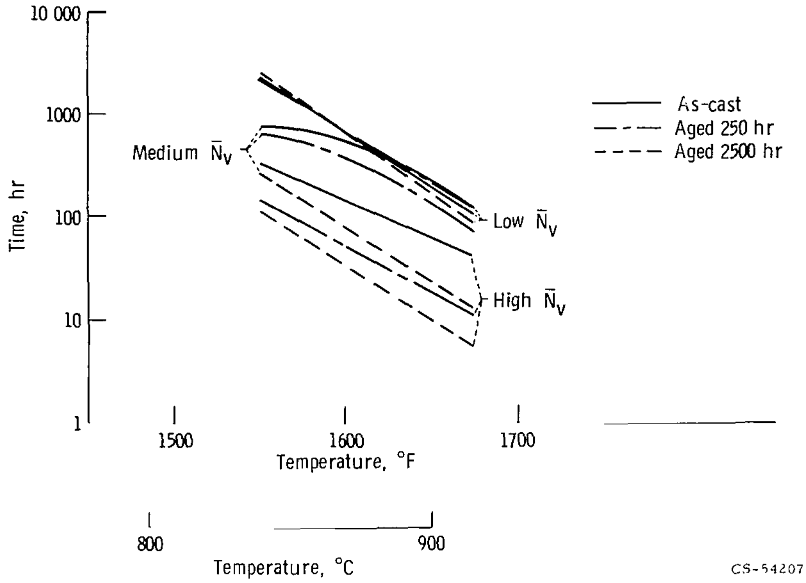


Figure 6. - Summary of stress rupture data. Exposed at 1550° F (843° C); test stress, 40 000 psi (276 MN/m^2).

prime reactions contribute to rupture life degradation. If this were true, then exposing all three alloys to sigma forming temperatures should have produced similar behavior when each of the alloys was tested after exposure. Our second hypothesis was that life degradation occurs only if the amount of sigma phase is changed while the material is under an applied stress. If this were true, then material exposed to form sigma should have behaved the same as as-cast material if both were tested so as to avoid formation or dissolving of the sigma phase. We assumed that the solubility of sigma decreases with decreasing temperature and that the exposure times used failed to achieve equilibrium. We therefore assumed that in sigma prone material, exposed 2500 hours at 1550° F (843° C), sigma would neither form nor dissolve appreciably during testing at 1575° F (857° C), a temperature slightly above the exposure temperature.

As will be shown, our data tend to reject both of the previous life degradation hypotheses. We suggest two alternate hypotheses: (1) sigma phase, or some change which is associated with the formation of sigma phase is responsible for rupture life degradation and, (2) the precipitation of sigma phase without applied stress, that is, before testing, is sufficient to shorten rupture life.

In figure 7 the 40 000 psi (276 MN/m^2) isostress curves show that exposed sigma free, low $\overline{N}_v$, alloy had as a minimum 79 percent of the life of as-cast material at 1675° F (913° C) and 40 000 psi (276 MN/m^2). Similarly the exposed moderately sigma prone, medium $\overline{N}_v$, alloy had a minimum of 10 percent, and the very sigma prone, high $\overline{N}_v$, alloy had a minimum of 14 percent of the lives of the as-cast alloy at the same

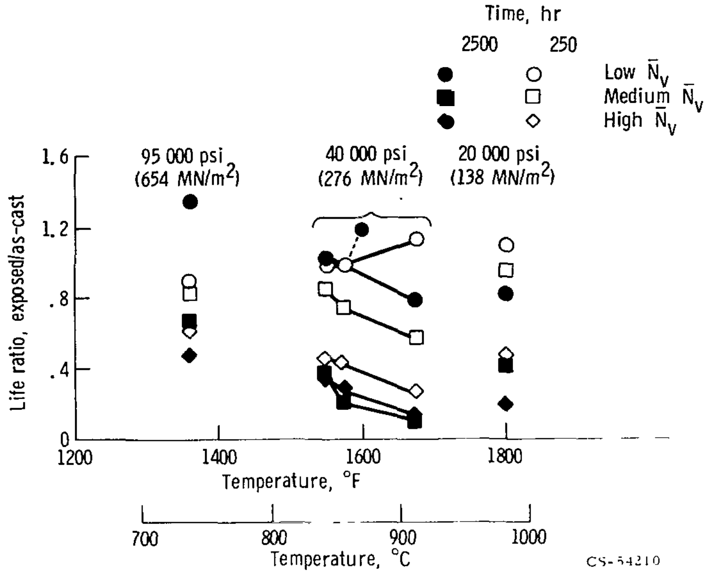


Figure 7. - Effect of exposure at 1550° F (843° C) on stress rupture life of cast IN-100.

testing conditions. For the sigma prone alloys, the increase in exposure time decreased rupture life. This was not always true of the sigma free alloy. Figure 7, then, indicates that exposure to 1550° F (843° C) prior to stress-rupture testing is severely degrading to the rupture life only in sigma prone alloys. This is believed sufficient for rejection of both of the initial hypotheses.

Plotting the data differently in figures 8 and 9 emphasizes the relation between composition and loss of rupture life. In these figures the rupture life at a specific test condition is normalized against the low $\bar{N}_v$ alloy having the same treatment. The high $\bar{N}_v$ alloy shows as little as 5 percent of the life of the low $\bar{N}_v$ alloy similarly treated, while

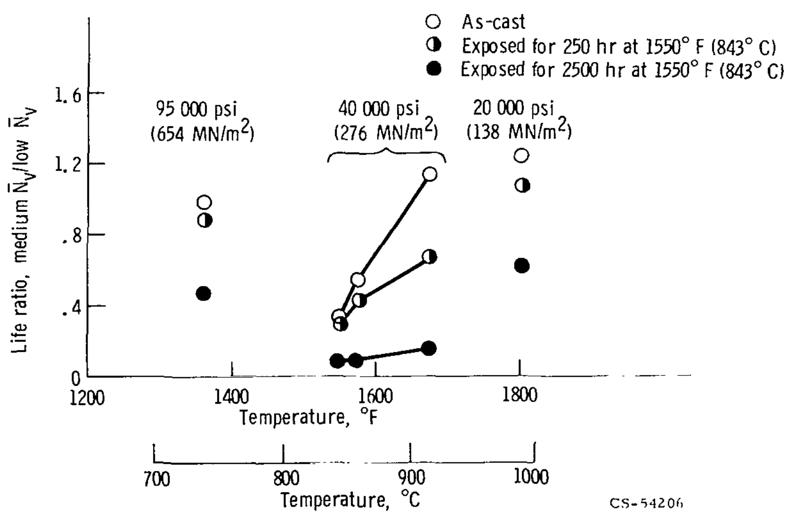


Figure 8. - Comparison of stress rupture lives of medium and low $\bar{N}_v$ IN-100.

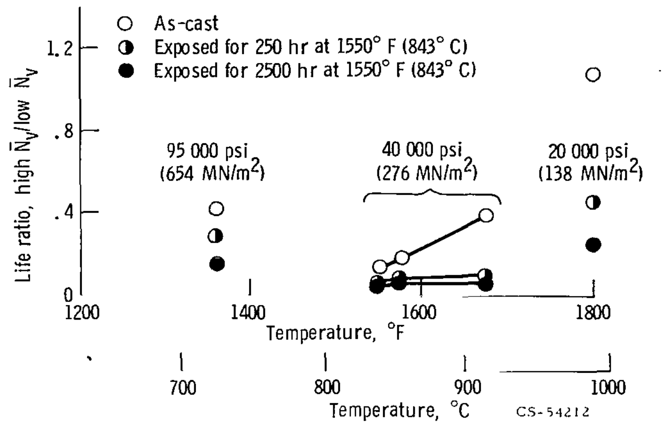


Figure 9. - Comparison of stress rupture lives of high and low $\overline{N}_v$ IN-100.

the medium $\overline{N}_v$ alloy has lives as short as 7 percent of low $\overline{N}_v$ alloy life. In the series of tests at 40 000 psi (276 MN/m^2) the life ratio increased with increasing temperature (decreasing test time).

If the life of IN-100 is related to the amount of sigma formed, as is strongly suggested by our data, then the medium $\overline{N}_v$ alloy aged 2500 hours should be similar in structure to the high $\overline{N}_v$ alloy aged 250 hours. Figure 4 shows this similarity. Further, the 40 000 psi (276 MN/m^2) data suggest that in the high $\overline{N}_v$ alloy little additional sigma precipitation occurred from 250 hours to 2500 hours. This too is shown in figure 4.

It appears from figure 4 that the greatest difference in microstructure among these materials is the increase in sigma from none in the sigma free alloy to the great quantities in the highly sigma prone alloy. In the low $\overline{N}_v$, sigma-free alloy, precipitation of a carbide along grain boundaries and adjacent to primary carbides is the major change which occurs with exposure at 1550° F (843° C). The etch used in figure 4 does not reveal changes in the gamma-gamma prime portion of the structure. As would be expected, however, gamma prime coarsening was observed to occur with longer exposure times.

We believe this work, particularly when viewed along with references 1, 2, and 6, conclusively shows that sigma formation in IN-100 can drastically shorten rupture life. Unfortunately, the reason why sigma formation shortens rupture life is not clear. It is generally agreed that Widmanstätten precipitates can seriously affect the ductility of alloys. We know of no such direct correlation with rupture life, but Guard (ref. 7) suggests that rupture ductility may in some cases control rupture life.

It has been suggested by Sims (ref. 8) that the cause of degradation of rupture life may be chemical in that strengtheners are removed from the gamma phase during sigma formation. Preliminary results obtained from analyses of electrolytically extracted residues in this laboratory suggest that the compositions of gamma prime in all three alloys after the material has been exposed 2500 hours at 1550° F (843° C) are similar. From our results we conclude that significant chemical change in the gamma, as suggested in reference 8, can only occur with simultaneous change in the relative amounts of gamma and gamma prime. This is required to maintain a mass balance in forming three phases from two phases holding the composition of one phase essentially constant. Sigma formation would then result in a change in the ratio of amount of gamma prime to gamma and a change in the composition of the gamma, but the gamma prime composition changes little. The suggestion that the composition of the gamma, but not of the gamma prime, changes implies that the lattice mismatch between those two phases also changes as sigma forms.

The combination of events which was just suggested offers three possible reasons for a decrease in stress rupture life. The first is that suggested by Sims in reference 8. Second, it has been suggested in references 9 and 10 that the best resistance to creep-rupture occurs when the lattice mismatch between gamma and gamma prime is near zero. If the change in mismatch is such that the absolute value of the mismatch increases, then a decrease in life would be expected. Finally, references 7, 9, and 10 suggest that an optimum ratio of gamma prime to gamma may exist and that it would be a ratio of approximately 1.5. IN-100 has been reported in reference 11 to have a gamma prime to gamma ratio near this value. Any change in gamma prime to gamma ratio would tend to be in the direction away from the optimum and a decrease in rupture life would be expected.

Another possible explanation for the decrease in rupture life with increasing sigma formation is that the formation of sigma cuts the grains into many smaller sections. These would then behave as fine grains. Hence a decrease in rupture life would be expected.

We have not established that any of these postulated mechanisms are responsible for the rupture life behavior observed in sigma prone IN-100. We are only citing a few plausible hypotheses concerning the mechanism of rupture life reduction which, perhaps, may eventually be accepted or rejected as additional evidence becomes available.

Unstressed Isothermal Transformation of Sigma Phase

In reference 2 the isothermal transformation curves for cast IN-100 were based on detecting sigma under polarized light after etching with mixed acids. A modified Murakami's etch revealed sigma in wrought IN-100 with less ambiguity than did the mixed acid etch. Polarized light was still used to identify sigma. Therefore, in order to compare cast and wrought IN-100, it was necessary to reexamine the cast IN-100 from reference 2, using Murakami's etch. No curves are shown for low $\overline{N}_v$ alloys because sigma was never observed in these alloys at times to 5000 hours and temperatures between 1300° and 1800° F (704° and 982° C).

Cast. - Figure 10 shows isothermal transformation curves for moderately and very sigma prone fine grained cast IN-100. The Murakami's etch revealed sigma in cast IN-100 in as little as one-tenth the exposure time for detecting sigma with the mixed acid etch, and the temperature of maximum sigma formation rate appeared to be higher than that reported in reference 2.

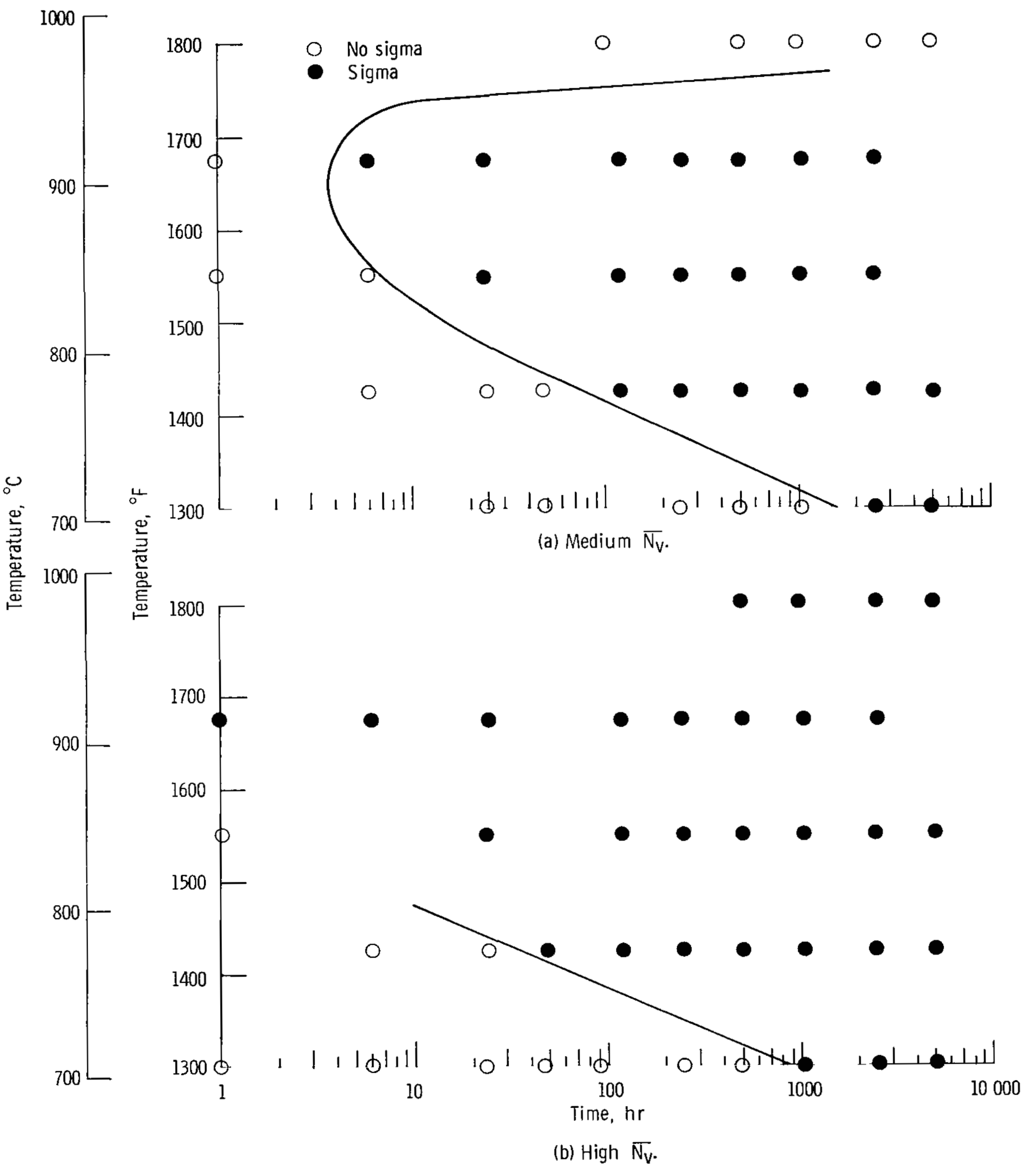


Figure 10. - Unstressed isothermal transformation of fine-grained cast IN-100.

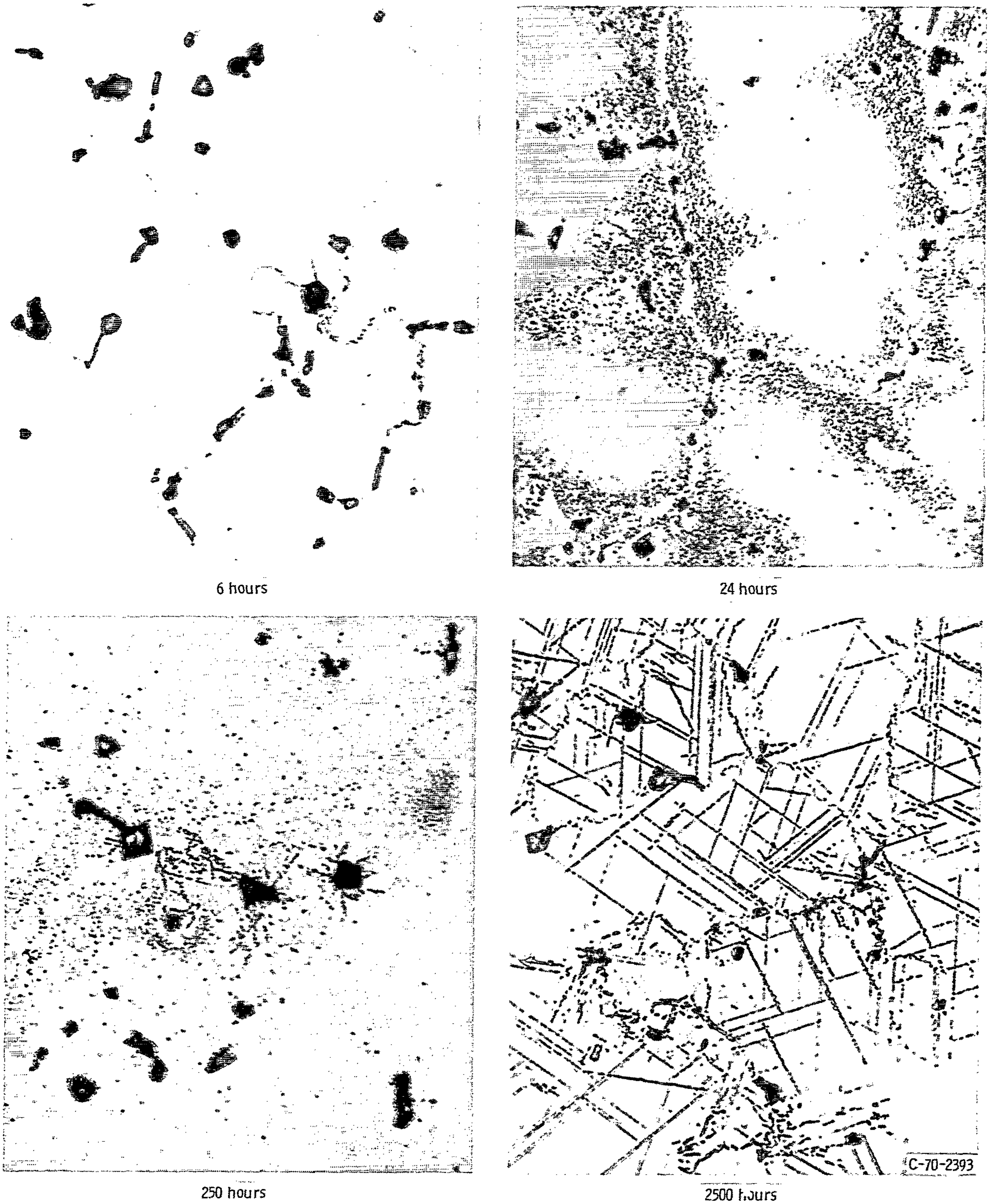


Figure 11. - Effect of exposure time at 1425° F (774° C) on medium $\bar{N}_V$ cast IN-100. Etchant, modified Murakami's solution; X750.

The criterion for sigma used in establishing these isothermal transformation curves was the observation of an optically active needlelike phase. A very fine constituent was observed with Murakami's etch that may be sigma but has not been identified as sigma by x-ray diffraction. However, its presence was not used to construct the isothermal transformation curves. This constituent occurred only in the sigma prone cast alloys and at temperatures below the nose of the transformation curve. The series of photomicrographs in figure 11 shows how the microstructure of moderately sigma prone cast IN-100 changes with time at 1425° F (774° C). At 6 hours the structure appears identical to the as-cast structure, except for a precipitate delineating the grain boundaries. At 24 hours a pepper and salt precipitate occurs in the matrix near the interdendritic regions. It is this structure that may be sigma phase or a metastable forerunner of sigma phase. It is not clearly revealed by the mixed acid etch which merely accentuates dendritic coring at this stage of exposure. After 250 hours needles of sigma are present in the region containing the pepper and salt precipitate, particularly in the vicinity of MC carbides. After 2500 hours, needles of sigma are clearly evident. However, they appear to be discontinuous and not as sharply defined as the sigma needles which form at higher temperatures.

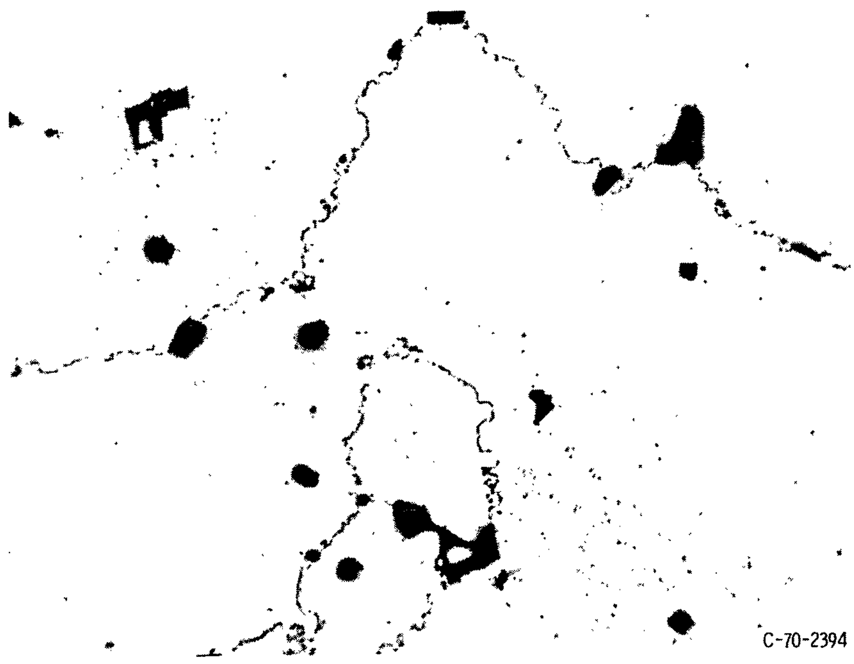
The low $\overline{N}_v$ alloy did not exhibit sigma needles, or the pepper and salt precipitate even after 5000 hours at 1425° F (774° C) or 1550° F (843° C). At 1425° F (774° C) figure 12 shows a matrix precipitate that may be related to the pepper and salt precipitate. At the higher temperature no matrix precipitate is visible. The chief difference revealed by the Murakami's etch between sigma free specimens exposed 5000 hours and as-cast is a grain boundary precipitate present after aging. The mixed acid etch revealed a general coarsening of the matrix gamma prime precipitate.

Wrought. - Figure 13 shows the isothermal transformation curves for medium and high $\overline{N}_v$ (moderately and highly sigma prone) wrought IN-100. Before isothermal exposure to form sigma, the wrought IN-100 was given a heat treatment as follows:

The three materials were first solution treated at 2200° F (1204° C) for 4 hours. This treatment did not fully dissolve the massive gamma prime in any of the alloys. This can be seen in figure 14. Sufficient gamma prime was dissolved in the low $\overline{N}_v$ alloy to permit considerable grain growth. The high and medium $\overline{N}_v$ alloys which contained substantial quantities of primary gamma prime showed a banded, duplex grain size. A three-step age at 2000°, 1550°, and 1400° F (1093°, 843°, and 760° C) followed the solution treatment. No sigma was observed in any alloy following this heat treatment.

A comparison of the isothermal transformation curves (figs. 10 and 13) for the cast and wrought moderately sigma prone IN-100 shows that sigma occurred later in the wrought alloy. In the highly sigma prone IN-100 sigma occurred sooner in the wrought alloy. Our expectation was that the working processes would homogenize the wrought IN-100 and delay the formation of sigma at both sigma prone $\overline{N}_v$ levels. If the pepper

(a) Temperature, 1550° F (843° C).



(b) Temperature, 1425° F (774° C).

Figure 12. - Effect of temperature on low $\bar{N}_V$ cast IN-100 exposed 5000 hours. Etchant, modified Murakami's solution; X750.

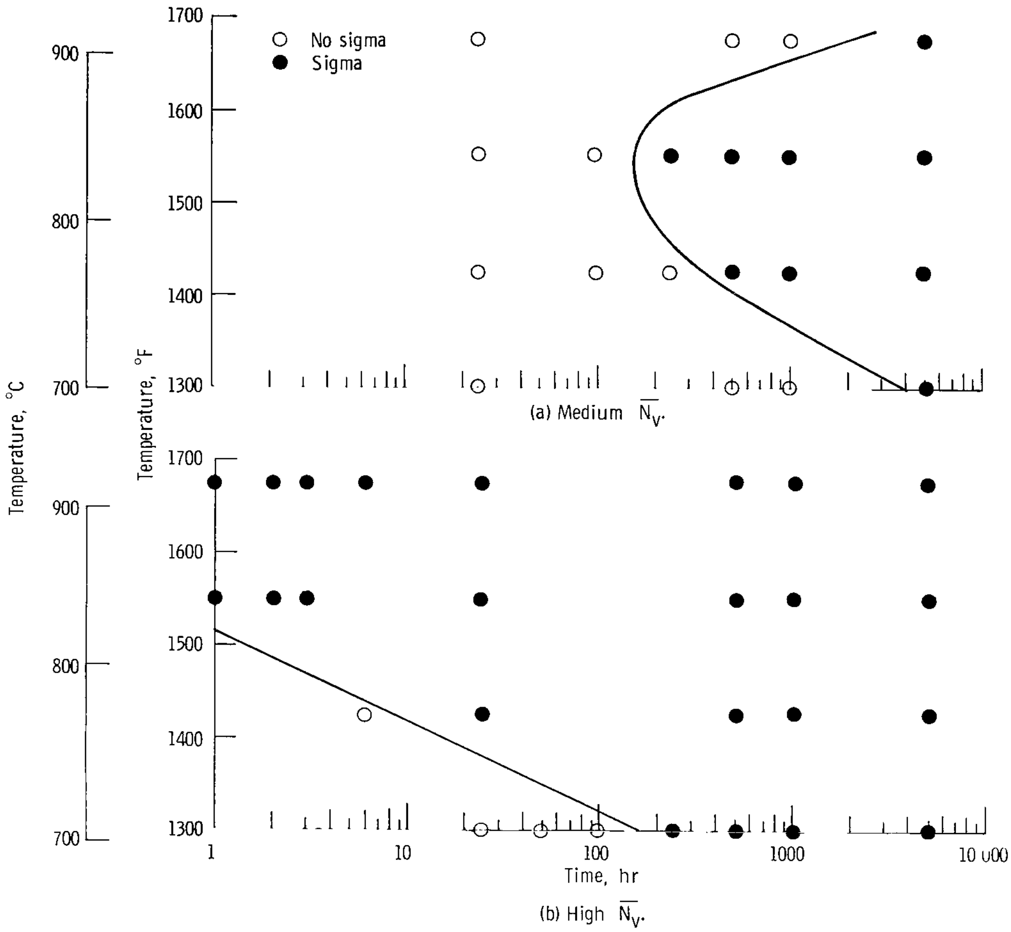
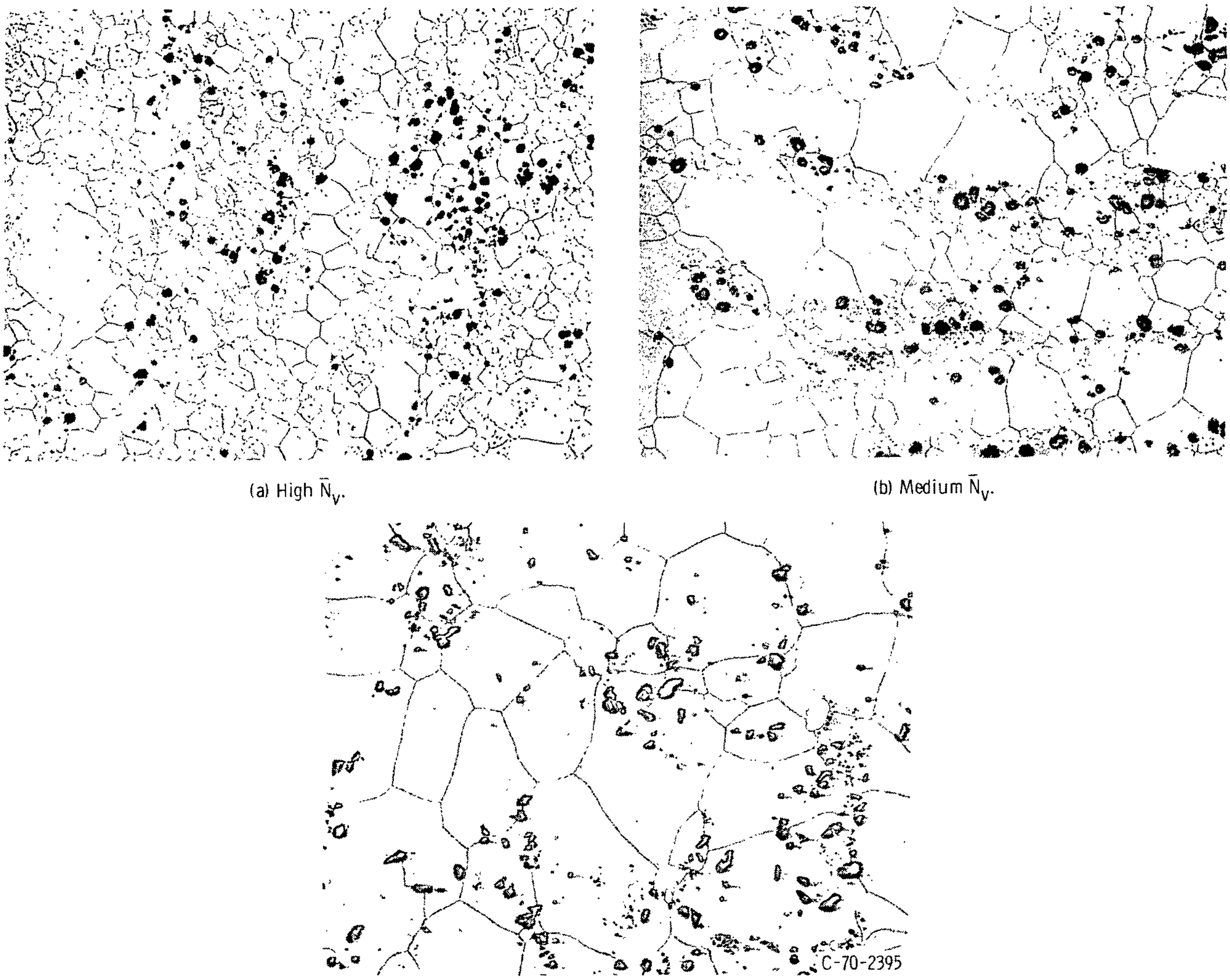


Figure 13. - Unstressed isothermal transformation of wrought IN-100.



(a) High $\bar{N}_V$.

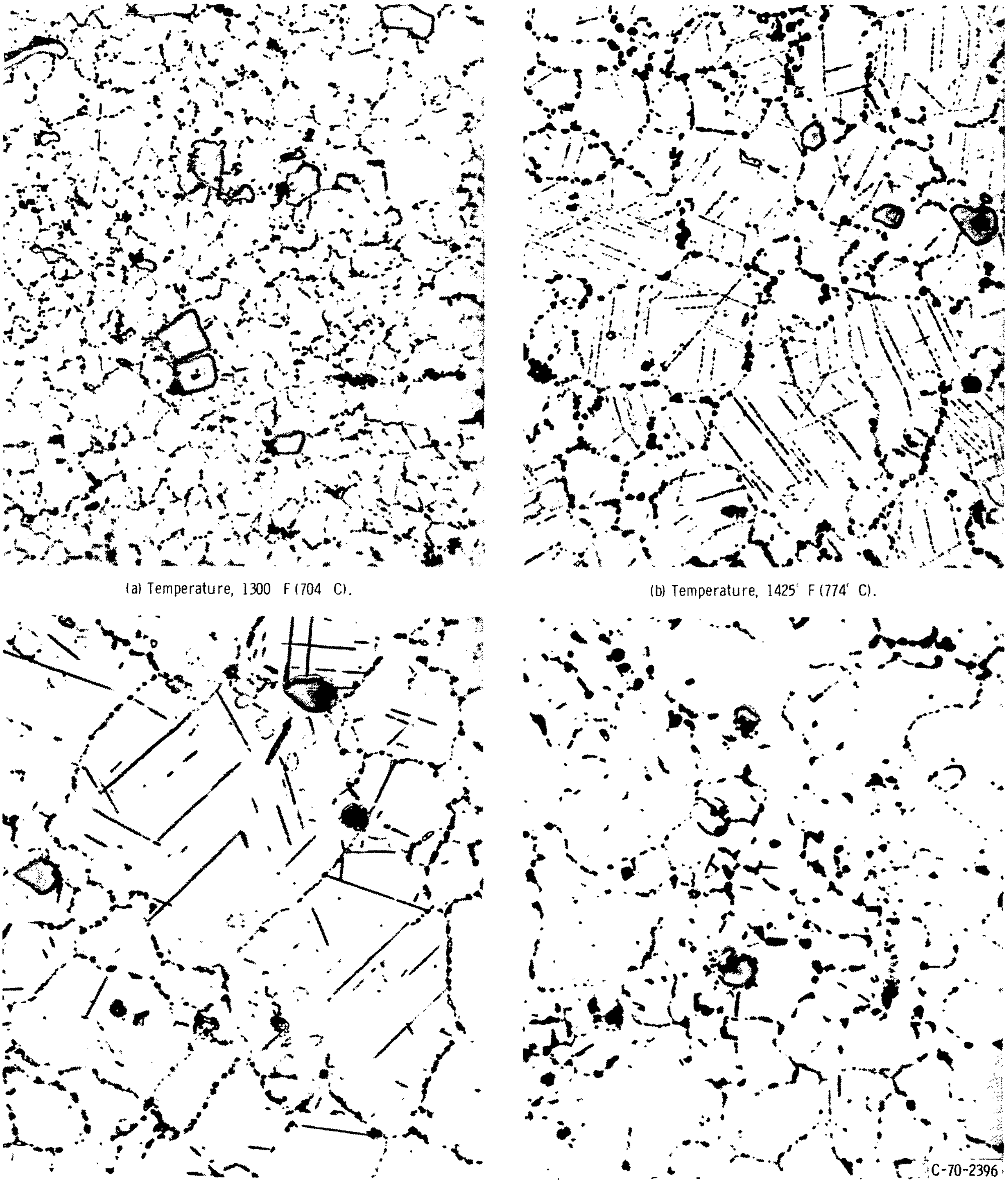
(b) Medium $\bar{N}_V$.

(c) Low $\bar{N}_V$.

Figure 14. - Effect of composition on wrought IN-100 solution treated at 2200° F (1204° C) for 4 hours. Etchant, mixed acids; X100.

and salt precipitate observed only in the cast material is interpreted as sigma, then both sigma prone wrought IN-100 alloys follow the expected behavior. We cannot rationalize the occurrence of sigma earlier in the wrought than in the cast form.

Figure 15 shows the effect of temperature on the microstructure of wrought moderately sigma prone IN-100. These microstructures developed as the result of exposure for 1000 hours at 1300°, 1425°, 1550°, and 1675° F (704°, 774°, 843°, and 913° C). No sigma was evident at 1675° or at 1300° F (913° or 704° C). At 1550° F (843° C) sigma needles were sharply defined. At 1425° F (774° C) the needles appeared to be discontinuous chains of precipitate.



(a) Temperature, 1300° F (704° C).

(b) Temperature, 1425° F (774° C).

(c) Temperature, 1550° F (843° C).

(d) Temperature, 1675° F (913° C).

Figure 15. - Effect of temperature on wrought medium $\bar{N}_V$ IN-100 exposed for 1000 hours. Etchant, modified Murakami's solution; X750.

Effect of Stress on Sigma Formation

Differences have been observed in the amount of sigma formed in the gage section and in the shoulders of sigma prone rupture specimens. These differences suggest a stress effect which we investigated with hourglass shaped specimens. Three specimens were exposed under load at combinations of two temperatures and two times. A 14 to 1 change in area provided a known stress gradient from the ends to the center of the specimens. A wrought moderately sigma prone specimen was exposed under a maximum stress of 35 000 psi (276 MN/m^2) at 1500° F (816° C) for 1008 hours. The most sigma was observed at low stresses in the axially sectioned specimen. When viewed metallographically the gradient in sigma appeared symmetrical: sigma decreased from the shoulders to the minimum diameter of the bar. An intercept count was made on micrographs (magnification, ×150) at 5 stresses (positions) from the center to one end of the bar with the result shown in table IV. A qualitative visual ranking of the same photomi-

TABLE IV. - EFFECT OF STRESS ON SIGMA

FORMATION AT 1500° F (816° C)

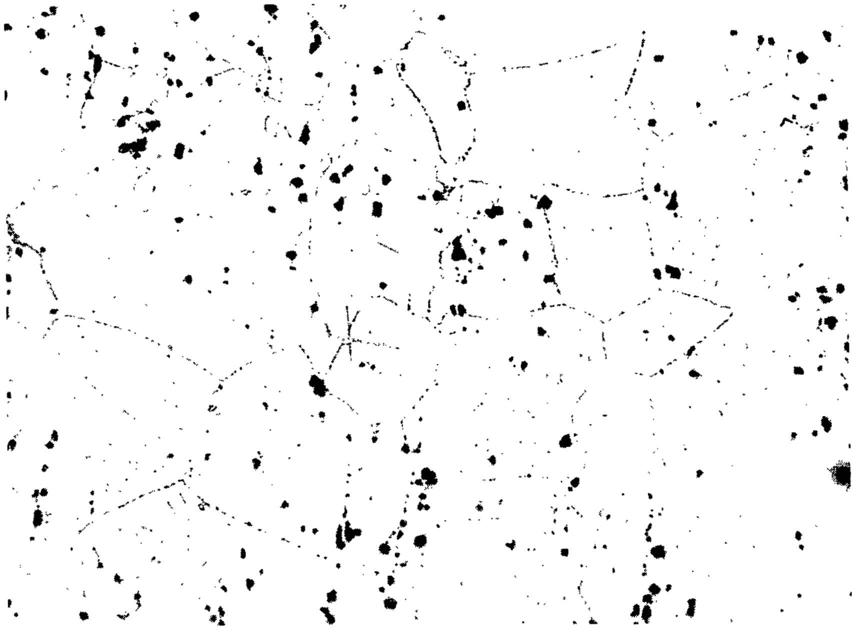
IN 1008 HOURS

Stress, psi (MN/m^2)	Sigma needle intercepts counted	[a]Qualitative ranking
35×10^3 (241)	9	2
29 (200)	6	1
15 (103)	21	3
4.2 (29)	12	4
2.5 (17)	39	5

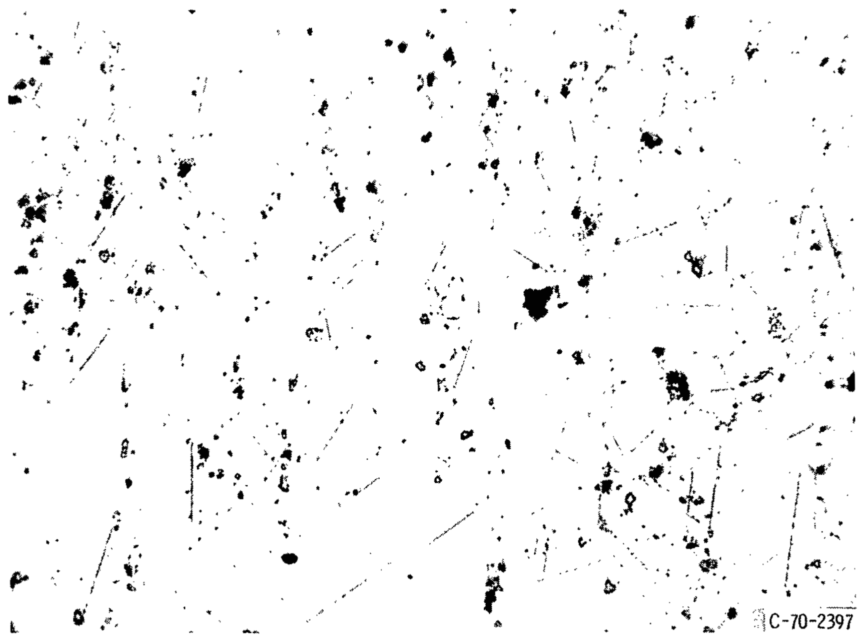
[a]Qualitative ranking is in order of increasing amount of sigma (5 appeared to contain the greatest amount and 1 the least).

crographs is also given in table IV and it shows that on this basis only one micrograph was not in the order of decreasing stress. Figure 16 shows photomicrographs of the regions stressed at 2500 and 35 000 psi (17 and 240 MN/m^2).

In the other two specimens considerably less sigma formed and the results were less clear-cut. The specimen exposed for 384 hours at 1550° F (843° C) with a maximum stress of 35 000 psi (241 MN/m^2) behaved similarly to the specimen exposed at 1550° F (816° C) for 1008 hours in that less sigma was observed near the maximum stress region than in the low stress ends.



(a) Stress, 35 000 psi (241 MN/m^2).



(b) Stress, 2500 psi (17.2 MN/m^2).

Figure 16. - Effect of stress on formation of sigma phase in medium $\bar{N}_v$ wrought IN-100 exposed 1008 hours at 1500° F (816° C). Etchant, modified Murakami's solution; X150.

These results substantiate that stress can influence the amount of sigma formed. In these two examples stress appears to have suppressed sigma formation. We have not determined the reason for this effect, although one possible explanation is that stress can affect the misfit between sigma nuclei and the lattice of the matrix. If that is the case, depending upon the sign of the misfit, stress could promote or suppress sigma nucleation, by decreasing or increasing coherency strains. In the third specimen, which was exposed at 1550° F (843° C) with a maximum stress of 21 000 psi (145 MN/m^2) for 1008 hours, a grain size effect may have over-ridden any effect due to stress. The average grain diameter roughly doubled from one end of the bar to the other. Sigma was present throughout the bar, but increased in amount as grain size decreased. These results suggest that the kinetics of the formation of sigma is affected by stress, but that other considerations such as working history or chemistry may have a greater influence on sigma precipitation kinetics.

SUMMARY OF RESULTS

Although sigma free IN-100 is now commercially available, sigma can form in material meeting AMS 5397, if the aluminum and titanium content are too high (high average electron vacancy concentration ($\overline{N}_V$)). For this investigation, sigma free, moderately sigma prone, and very sigma prone (low, 2.27 to 2.31; medium, 2.47 to 2.51; and high $\overline{N}_V$, 2.59 to 2.71) IN-100 were prepared by making additions of aluminum and titanium to a single master heat of IN-100. The effect on mechanical properties of heating at 1550° F (843° C) for 250 and 2500 hours to permit sigma to form before testing was investigated with fine grained investment cast specimens. Isothermal transformation curves without applied stress were established for cast IN-100 and wrought alloys having compositions similar to IN-100. The effect of stress on sigma formation was examined with the aid of hourglass shaped tensile specimens.

The following major results emphasize the effect of sigma formation on mechanical properties of fine grained cast IN-100 after exposure at 1550° F (843° C) prior to testing:

1. Room temperature ultimate tensile strength and ductility decreased with exposure time at 1550° F (843° C) for all three compositions.

2. After exposure for 2500 hours at 1550° F (843° C), ultimate tensile and yield strength and percent elongation all decreased with increasing tendency toward sigma formation.

3. Although the effect of sigma formation on ultimate tensile strength at 1400° F (760° C) was slight, exposure to 1550° F (843° C) usually decreased strength. Ductility of sigma free IN-100 increased with exposure time while that of sigma prone IN-100 generally decreased with exposure time.

4. At 1400° F (760° C) increasing the tendency toward sigma formation resulted in lower ductility after exposure to 1550° (843° C).

5. The longer the sigma prone IN-100 specimens were exposed to 1550° F (843° C) before testing, the more stress rupture life was degraded in tests at temperatures from 1360° to 1800° F (738° to 982° C).

6. The greater the sigma forming tendency, the more a given exposure at 1550° F (843° C) degraded the rupture life of cast IN-100.

Comparison of isothermal transformation diagrams for cast fine grain size IN-100 and wrought alloys of similar compositions suggests that when onset of sigma was defined as the first appearance of a needlelike constituent, sigma occurred sooner in wrought high $\overline{N}_v$ (2.59) alloy and later in wrought medium $\overline{N}_v$ (2.40) alloy than in their cast counterparts. However, a pepper and salt precipitate, which occurred only in cast IN-100 at temperatures below the nose of the isothermal transformation curve, may more truly represent the onset of sigma. If that is the case, sigma forms later in both the high and medium $\overline{N}_v$ wrought alloys than in cast IN-100, as would be expected of the more homogeneous wrought material.

Metallographic examination of hourglass shaped tensile specimens showed that when wrought medium $\overline{N}_v$ IN-100 was exposed for 1008 hours at 1500° F (816° C) under stresses from 2500 to 35 000 psi (17 to 241 MN/m^2), increasing stress suppressed sigma formation. However, in a specimen in which grain size increased from one end to the other, sigma formation increased as grain size decreased, masking any stress effect.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, July 23, 1970,
129-03.

REFERENCES

1. Ross, E. W.: René 100: A Sigma-Free Turbine Blade Alloy. J. Metals, vol. 19, no. 12, Dec. 1967, pp. 12-14.

2. Dreshfield, Robert L.; and Ashbrook, Richard L.: Sigma Phase Formation and its Effect on Stress-Rupture Properties of IN-100. NASA TN D-5185, 1969.

3. Anon.: Alloys Casting, Investment, Corrosion and Heat Resistant, Nickel Base-10Cr-15Co-3Mo-4.75Ti-5.5Al-0.95V, Vacuum Melted and Vacuum Cast. Aerospace Material Spec. No. 5397, Feb. 15, 1965.

4. Boesch, William J.; and Slaney, John S.: Preventing Sigma Phase Embrittlement in Nickel Base Superalloys. Metal Progress, vol. 86, no. 1, July 1964, pp. 109-111.

5. Anon.: High Temperature High Strength Nickel Base Alloys. International Nickel Co., Inc., 1964.

6. Wlodek, S. T.: The Structure of IN-100. Trans. ASM, vol. 57, no. 1, Mar. 1964, pp. 110-119.

7. Guard, Ray W.: Alloying for Creep Resistance. Mechanical Behavior of Materials at Elevated Temperatures. John E. Dorn, ed., McGraw-Hill Book Co., Inc., 1961, pp. 270-287.

8. Sims, Chester T.: A Contemporary View of Nickel-Base Superalloys. J. Metals, vol. 18, no. 10, Oct. 1966, pp. 1119-1130.

9. Pridantsev, M. V.: Heat-Resisting Ageing Alloys Based on Nickel or Iron. Russian Metallurgy (Metally), no. 5, 1967, pp. 14-18.

10. Davies, R. G.; and Johnston, T. L.: The Metallurgical Design of a Superalloy. Presented at Third Bolton Landing Conference on Intermetallic Compounds, Their Alloys, Ordering, and Physical Metallurgy, Bolton Landing, N.Y., Sept. 8-10, 1969.

11. Kriege, Owen H.; and Baris, J. M.: The Chemical Partitioning of Elements in Gamma Prime Separated from Precipitation-Hardened, High-Temperature Nickel-Base Alloys. Trans. ASM, vol. 62, no. 1, Mar. 1969, pp. 195-200.

NASA-Langley, 1970 —— 17 E-5821